Designation: D6832 – 13ε1

Standard Test Method for the Determination of Hexavalent Chromium in Workplace Air by Ion Chromatography and Spectrophotometric Measurement Using 1,5-diphenylcarbazide[1]

This standard is issued under the fixed designation D6832; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

ε[1] NOTE—Editorial corrections were made in October 2013.

1. Scope

1.1 This test method specifies a method for the determination of the time-weighted average mass concentration of hexavalent chromium in workplace air samples.

1.2 The method is applicable to the personal sampling of the inhalable fraction of airborne particles, as defined in ISO 7708, and to area (static) sampling.

1.3 The sample dissolution procedure specifies separate procedures for soluble and insoluble hexavalent chromium.

1.4 The method is applicable to the determination of masses of 0.01 µg to 10 µg of hexavalent chromium per sample without dilution.

1.5 The concentration range for hexavalent chromium in air for which this procedure is applicable is approximately 0.1 µg/m^3 to 100 µg/m^3, assuming 1 m^3 of air sample. The range can be extended upwards by appropriate dilution.

1.6 Interconversion of trivalent and hexavalent chromium species may occur during sampling and sample preparation, but these processes are minimized to the extent possible by the sampling and sample preparation procedures employed.

1.7 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.8 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D3195 Practice for Rotameter Calibration

D4840 Guide for Sample Chain-of-Custody Procedures

E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

E1370 Guide for Air Sampling Strategies for Worker and Workplace Protection

2.2 *ISO Standards:*[3]

ISO 648 Laboratory Glassware—One-mark Pipets

ISO 1042 Laboratory Glassware—One-mark Volumetric Flasks

ISO 3585 Glass Plant, Pipeline and Fittings—Properties of Borosilicate Glass 3.3

ISO 7708 Air Quality—Particle Size Definitions for Health-related Sampling

ISO 8655 Piston and/or Plunger-operated Volumetric Apparatus (6 Parts)

3. Terminology

3.1 For definitions of terms used in this standard test method, refer to Terminology D1356.

4. Summary of Test Method

4.1 A known volume of air is drawn through a filter to collect particulate hexavalent chromium. The sampler is designed to collect the inhalable fraction of airborne particles (see ISO 7708).

4.2 The filter and collected sample are subjected to a dissolution procedure in order to extract hexavalent chromium.

[1] This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.04 on Workplace Air Quality.

Current edition approved Oct. 1, 2013. Published October 2013. Originally approved in 2002. Last previous edition approved in 2008 as D6832 – 08. DOI: 10.1520/D6832-13E01.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

The sample dissolution procedure may consist of one (or both) of two techniques: one for soluble and one for insoluble hexavalent chromium.

NOTE 1—If it is desired to measure both soluble as well as total hexavalent chromium, the soluble procedure is used first, and this is followed by the procedure for insoluble hexavalent chromium compounds. Thus, total Cr[VI] is the sum of soluble and insoluble hexavalent chromium compounds. On the other hand, if it is desired to measure total hexavalent chromium without first isolating insoluble Cr[VI] compounds, only the procedure for insoluble Cr[VI] is required (this will dissolve both soluble and insoluble hexavalent chromium compounds).

4.2.1 For dissolution of soluble hexavalent chromium, distilled water with no heating is used to treat the sample. Alternatively, a weakly basic ammonium sulfate/ammonium hydroxide buffer solution with no heating is used to extract soluble forms of hexavalent chromium.

4.2.2 For dissolution of insoluble hexavalent chromium, a basic carbonate buffer solution with heating by a hot plate is used for sample treatment. Alternatively, an ultrasonic bath is used instead of a hot plate.

4.3 Aliquots of sample extracts are subjected to ion chromatography in order to separate extracted hexavalent chromium from trivalent chromium and other metal cations. An ammonium sulfate/ammonium hydroxide eluent solution is used as the mobile phase.

4.4 Following separation, hexavalent chromium is reacted with an acidic solution of 1,5-diphenylcarbazide to form a characteristic violet chromium-diphenylcarbazone complex. Post-column derivatization is used in order to react hexavalent chromium with 1,5-diphenylcarbazide.

4.5 The absorbance of the chromium-diphenylcarbazone complex is measured at 540 nm using visible spectrophotometry. Analytical results are obtained by plotting the measured absorbance as a function of concentration of the chromium-diphenylcarbazone complex.

4.6 The analysis results may be used for the assessment of workplace exposures to hexavalent chromium in air.

5. Significance and Use

5.1 Airborne hexavalent chromium is carcinogenic (**1**),[4] and analytical methods for the measurement of this species in workplace aerosols are desired. Worker exposure to hexavalent chromium occurs primarily through inhalation (**1**), and this test method provides a means for exposure assessment to this highly toxic species. Analytical results from this procedure can be used for regulatory compliance purposes (**2**).

6. Reactions

6.1 Reduction of hexavalent chromium to trivalent species can occur in acidic environments, and also in the presence of organic material or environments having high iron concentrations in air (**3**). Reduction of hexavalent chromium can also occur on filter media (**4**), and efforts should to taken to minimize this contribution to sample loss. Oxidation of trivalent chromium to hexavalent species can occur in strong base and in the presence of air (**5**), so efforts should be taken to minimize these contributions to analytical bias. In plating mist samples and in some welding fume samples, interference from iron may be problematic (**3**).

7. Apparatus

7.1 *Samplers,* designed to collect the inhalable fraction of airborne particles, for use when the exposure limits of interest apply to the inhalable fraction of airborne particles (as defined in ISO 7708).

NOTE 2—In general, personal samples for collection of the inhalable fraction of airborne particles do not exhibit the same size selective characteristics if used for area (static) sampling.

NOTE 3—Consider whether the sample is meant to constitute only that material which is collected on filter material, or whether the sample comprises all particulate that is captured within the sampler (that is, all material on the filter, backup pad (if applicable), and on the inside walls of the sampler). See Appendix X1 for guidance on handling of wall deposits within sampling cassettes.

7.2 *Filters,* of a diameter suitable for use with the samplers (7.1), with a collection efficiency of not less than 99.5 % for particles with a 0.3 µm diffusion diameter (ISO 7708), and compatible with the sample preparation and analysis method.

NOTE 4—Typical filter diameters for personal sampling are 25 mm and 37 mm.

7.2.1 Filters should not react with Cr(VI). The following are acceptable:

7.2.1.1 *Polyvinyl Chloride (PVC) Membrane Filters*, 5 µm pore size or below.

7.2.1.2 *Polyvinyl Fluoride (PVF) Membrane Filters*, 5 µm pore size or below.

7.2.1.3 *Polytetrafluorinated Ethylene (PTFE) Membrane Filters*, 5 µm pore size or below.

7.2.1.4 *Glass Fiber Filters*, binder-free.

7.2.1.5 *Quartz Fiber Filters.*

7.2.1.6 *PVC/Acrylic Copolymer Membrane Filters*, 5 µm pore size or less.

NOTE 5—Several types of filters have been found to cause reduction of hexavalent chromium (**4**). Mixed cellulose ester (MCE) filters may cause significant reduction of hexavalent chromium, and are generally unsuitable. Some PVC filters have been reported to cause hexavalent chromium reduction; this should be investigated prior to choosing PVC filters.

NOTE 6—When sampling chromic acid mist, there is an advantage if the oxidizing potential of hexavalent chromium is lowered, for instance by impregnating the filter with alkali. For example, this can be accomplished by soaking the filter overnight in 1 M sodium hydroxide, and allowing it to dry. This lessens the tendency of Cr(VI) to react with organic compounds in the filter material, or reducing agents and dust present in the sampled air, or both. Filter materials such as PVC and PTFE can be unsuitable for alkali treatment since they tend to be hydrophobic and therefore not easily wetted. PVF and vinyl/acrylic copolymer membrane filters have been found to be suitable for alkali treatment (**3**).

7.3 *Backup Pads,* if necessary for use in the particular sampler employed.

NOTE 7—Cellulose backup pads should not be used for sampling of chromic acid mist, since droplets can penetrate the filter by capillary force, resulting in the possibility of Cr(VI) reduction with the backup pad material. Glass or quartz fiber backup pads could be used, or a mesh comprised of material that is resistant to chromic acid.

[4] The boldface numbers in parentheses refer to the list of references at the end of this test method.

7.4 *Sampling Pumps,* with an adjustable flow rate and capable of maintaining the selected flow rate (between 1 and 5 L/min for personal sampling pumps, and between 5 and 400 L/min for high-volume sampling pumps) to within ±5 % of the nominal value throughout the sampling period (up to 8-10 h for personal sampling, or shorter periods for high-volume sampling). For personal sampling the pumps shall be capable of being worn by the worker without impeding normal work activity. Sampling pump flow rates shall be set using either a primary or secondary standard; if a secondary standard is used, it shall be calibrated using a primary standard (see D3195).

NOTE 8—A flow-stabilized pump may be required to maintain the flow rate within the specified limits.

7.5 *Flowmeter, Portable,* capable of measuring the selected volumetric flow rate to within ±2 %, and calibrated against a primary standard (that is, a flowmeter whose accuracy is traceable to primary standards).

7.6 *Ancillary Equipment:*

7.6.1 *Flexible Tubing,* of a diameter suitable for making a leak-proof connection from the sampler to the sampling pump.

7.6.2 *Belts or Harnesses,* to which the sampling pump can be conveniently fixed for personal sampling (except where sampling pumps are small enough to fit inside workers' pockets).

7.6.3 *Flat-Tipped Forceps,* plastic or plastic-tipped, for loading and unloading filters into or out of samplers.

7.6.4 *Filter Transport Cassettes,* or similar, if required, in which to transport samples for laboratory analysis.

7.6.5 *Disposable gloves,* for sample handling and prevention of sample contamination.

7.7 *Analytical or Laboratory Apparatus*

Ordinary laboratory apparatus, and:

7.7.1 *Glassware,* made of borosilicate glass 3.3 and complying with the requirements of ISO 3585.

7.7.1.1 *Beakers,* of capacities between 50 mL and 2 L.

7.7.1.2 *Watch Glasses,* to fit the beakers.

7.7.1.3 *One-Mark Pipets,* complying with the requirements of ISO 648.

7.7.1.4 *One-Mark Volumetric Flasks,* of capacities between 10 mL and 1000 mL, complying with the requirements of ISO 1042.

7.7.1.5 *Piston-Operated Volumetric Apparatus,* complying with the requirements of ISO 8655. Pipettors, as an alternative to one-mark pipets for the preparation of standard solutions, calibration solutions, and dilution of samples. Dispensors, for dispensing acids.

7.7.2 *Hot Plate,* thermostatically controlled, capable of maintaining a surface temperature of approximately 135°C; for hot plate extraction of insoluble hexavalent chromium compounds.

7.7.3 *Sonicator,* minimum power output 0.5 W/cm^2, for use in the ultrasonic extraction of insoluble hexavalent chromium compounds.

7.7.4 *Ion Chromatograph,* having the following components:

NOTE 9—The following components should be comprised, to the extent possible, of inert materials.

7.7.4.1 *Pump,* capable of delivering a constant flow in the range of 1 to 5 mL/min at a pressure of 15 to 150 MPa.

7.7.4.2 *Injection Valve*—A low dead-volume valve, (1 mL or less), nonmetallic, that will allow the loading of sample contents into the eluant stream. Sample loops of up to 1 mL volume will provide enhanced detection limits.

NOTE 10—Either an autosampler or a manual injection system, or both, is (are) acceptable.

7.7.4.3 *Guard Column*—A column placed before the separator column (7.7.4.4) to protect the separator column from fouling by particles or strongly adsorbed organic constituents.

7.7.4.4 *Separator Column*—A column packed with high capacity pellicular anion exchange resin that is suitable for resolving hexavalent chromium from other metals and cations.

7.7.4.5 *Reagent Delivery Module*—A device capable of delivering 0 to 2 mL/min of reagent solution against a back pressure of up to 40 kPa.

7.7.4.6 *Mixing Tee and Reaction Coil*—A device capable of mixing two flowing streams with minimal band spreading.

7.7.4.7 *Detector*—A low-volume flow-through visible absorbance detector with a nonmetallic flow path.

7.7.4.8 *Recorder, Integrator or Computer*—A device compatible with detector output, capable of recording detector response as a function of time for the purpose of measuring peak height or area.

NOTE 11—The use of an automated system is recommended.

7.7.5 *Eluant Reservior*—A container suitable for storing eluant solution.

7.7.6 *Syringe Filter,* 0.45 µm, for sample filtration prior to analysis. The filter material shall be chemically inert.

7.7.7 *Syringe,* equipped with a male fitting and a capacity of at least 1 mL; or auto sampler module with like specifications.

8. Reagents

8.1 For the analysis of hexavalent chromium, use only reagents of recognized analytical grade, and only water as specified in (8.1.1).

8.1.1 *Water,* complying with the requirements of ASTM Type 1 water (as specified in Specification D1193: electrical conductivity less than 0.1 mS/m and resistivity greater than 0.01 M-Ω-m at 25°C).

8.1.2 *Sulfuric acid (H_2SO_4),* concentrated, specific gravity ~1.84 g/mL, ~98 % (m/m).

8.1.3 *Nitric aAcid (HNO_3),* concentrated, specific gravity ~1.42 g/mL, 69-71 % (m/m).

8.1.4 *Nitric acid wash solution (1 % HNO_3)*—Dilute 10 mL of concentrated nitric acid (8.1.3) to 1 litre with water (8.1.1).

8.1.5 *Sodium carbonate (Na_2 CO_3),* anhydrous, purity greater than 99.9 % (m/m).

8.1.6 *Sodium hydroxide (NaOH),* pellets, purity greater than 99.5 % (m/m).

8.1.7 *Ammonium sulfate ($(NH_4)_2SO_4$),* purity greater than 99.5 % (m/m).

8.1.8 *Ammonia (NH_3),* concentrated, specific gravity ~0.90 g/mL, ~29 % (m/m).

8.1.9 *1,5-diphenylcarbazide ($C_6H_5NHNHCONHNHC_6H_5$),* purity greater than 98 % (m/m).

8.1.10 *Methanol (CH_3OH),* HPLC grade.

8.1.11 *Potassium dichromate ($K_2Cr_2O_7$),* purity greater than 99.9 % (m/m).

8.1.12 *Extraction solutions.*

NOTE 12—Extraction solutions other than those specified may be used, if desired, provided that it can be demonstrated that the performance of the measuring procedure is not impaired.

8.1.12.1 *Extraction solution for insoluble Cr(VI) compounds,* 2 % (m/v) sodium hydroxide/3 % (m/v) sodium carbonate: Dissolve 20 g of sodium hydroxide pellets (8.1.6) and 30 g of sodium carbonate (8.1.5) in 250 mL of water (8.1.1), swirl to mix, and allow to cool. Quantitatively transfer the solution to a one litre volumetric flask, dilute to the mark with water (8.1.1), stopper and mix thoroughly.

8.1.12.2 Extraction solutions for soluble Cr(VI) compounds, either of the following:

(1) Water (8.1.1), or

(2) Extraction buffer, ammonium sulfate/ammonium hydroxide buffer solution (0.05 M $(NH_4)_2SO_4$/0.05 M NH_4OH, pH ~8): Dissolve 6.6 g of ammonium sulfate ($(NH_4)_2SO_4$) (8.1.7) in about 500 mL of water. Add 3.25 mL of concentrated ammonium hydroxide (NH_4OH) (8.1.8). Mix well and dilute to 1 litre with water (8.1.1) in a one-mark volumetric flask. Stopper and mix thoroughly.

NOTE 13—This extraction buffer will dissolve water-soluble Cr(VI), for example, potassium chromate, and it may dissolve Cr(VI) compounds which are not water-soluble, for example, strontium chromate. However, this buffer will not dissolve insoluble Cr(VI) compounds such as lead chromate and barium chromate. The use of this extraction buffer serves to stabilize chromium species in solution (for example, trivalent and hexavalent) and thereby reduces interconversion rates of trivalent and hexavalent chromium valence states.

8.1.13 *Eluant Solutions:*

8.1.13.1 *Eluant concentrate,* 2.0 M ammonium sulfate, $(NH_4)_2SO_4$/1 M ammonium hydroxide, NH_4OH: Dissolve 264 g of ammonium sulfate ($(NH_4)_2SO_4$) (8.1.7) in about 500 mL of water. Add 65 mL of concentrated ammonium hydroxide (NH_4OH) (8.1.8). Mix well and dilute to 1 litre with water (8.1.1) in a one-mark volumetric flask. Stopper and mix thoroughly.

8.1.13.2 *Eluant solution,* 0.20 M ammonium sulfate, $(NH_4)_2SO_4$/0.1 M ammonium hydroxide, NH_4OH: Add 100 mL of eluant concentrate (8.1.13.1) to a 1-litre one-mark volumetric flask and dilute to volume with water (8.1.1). Stopper and mix thoroughly.

8.1.14 *pH Indicator papers,* suitable for measuring the pH of sample solutions (pH 8.0 ± 0.5) and the pH of effluent from the spectrophotometric detector (pH 2.0 or lower).

8.1.15 *Hexavalent Chromium Standard Solutions:*

8.1.15.1 *Hexavalent Chromium Stock Standard Solution (~1000 µg Cr/l)*—Use a commercially available hexavalent chromium standard solution with a certified concentration. Observe the manufacturer's expiration date or recommended shelf life. Alternatively, dissolve 0.2828 g of potassium dichromate ($K_2Cr_2O_7$) (which has been dried at 105°C for 1 h and then cooled in a dessicator) in water (8.1.1). Dilute with water (8.1.1) to 100 mL in a one-mark volumetric flask, stopper and mix thoroughly.

NOTE 14—Potassium chromate (K_2CrO_4) can be used as an alternative to potassium dichromate for the preparation of hexavalent chromium standard solutions.

8.1.15.2 *Hexavalent Chromium Working Standard Solution (1000 µg Cr/l)*—Pipet 1.00 mL of the chromium stock solution (8.1.15.1) into a 1-litre one-mark volumetric flask and dilute to volume with water (8.1.1). Stopper and mix thoroughly. Prepare this solution fresh monthly.

8.1.15.3 *Hexavalent Chromium Calibration Solutions*—Prepare a minimum of five calibration solutions in the concentration range of 0.02 to 5 µg/L by diluting appropriate pipetted volumes of the 1000 µg/L standard solution (8.1.15.2) in the appropriate extraction solution (8.1.12). Prepare these solutions fresh daily.

8.1.16 *1,5-Diphenylcarbazide Reagent Solution*—Dissolve 0.125 g of 1,5-diphenylcarbazide (8.1.9) in 25 mL of methanol (8.1.10). Add about 100 mL of water (8.1.1) containing 5.6 mL of concentrated sulfuric acid (8.1.2). Dilute with water (8.1.1) to 250 mL in a one-mark volumetric flask, stopper and mix thoroughly. Prepare this solution fresh daily.

NOTE 15—Other suitable solvents, such as acetone, may be used for the preparation of the 1,5-diphenylcarbazide reagent solution (if desired).

9. Sampling

NOTE 16—For information on strategies for the sampling of workplace atmospheres, consult Guide E1370.

9.1 *Sampling Procedure:*

9.1.1 *Selection and Use of Samplers:*

9.1.1.1 Select a sampler designed for collection of the inhalable fraction of airborne particles, as defined in ISO 7708.

NOTE 17—If possible, samplers selected should be manufactured from conducting material, since samplers comprised of non-conducting material have electrostatic properties that can adversely influence representative sampling.

9.1.1.2 Use the samplers at their designed flow rate (between 1 and 5 L/min), and in accordance with the manufacturer's instructions, so that they collect the inhalable fraction of airborne particles.

9.1.2 *Sampling Period:*

9.1.2.1 Select a sampling period long enough to ensure that the amount of hexavalent chromium collected is adequate to enable hexavalent chromium in air concentrations to be determined at the required level (see Guide E1370). Ideally, the sampling period should be for the entire workday.

9.1.2.2 In calculating the minimum sampling time required it is necessary to consider the selected flow rate and the lower limit of the recommended analytical working range of the method.

9.1.2.3 The sampling time shall not be so long as to risk overloading of the filter with particulate material. This is a concern when high concentrations of hexavalent chromium in air are anticipated.

NOTE 18—If filter overloading is an observed or suspected problem and it is desired to sample for the entire workday, it may be necessary to collect consecutive samples.

9.2 *Preparation of Sampling Equipment:*

9.2.1 Perform the following in an area where contamination from hexavalent chromium is known to be at a minimum:

9.2.1.1 Clean the samplers before use by soaking them in detergent solution, rinsing them thoroughly with water, and then drying them.

9.2.1.2 Load the filters into clean, dry samplers. Handle the filters only with clean flat-tipped forceps and gloved hands. Seal each loaded filter with tape or shrink-wrap in order to secure the individual sections of the sampler. Cap the inlet and outlet of each sampler with a cover or plug to protect the filter and interior of the sampler from contamination.

NOTE 19—Samplers that are pre-loaded with filters are available commercially from a number of vendors.

9.2.1.3 Remove the protective cover or plugs from a loaded sampler. Connect the sampling pump to the loaded sampler using flexible tubing, and ensure that there are no leaks. Turn on the pump, and allow for an appropriate warm-up period (if necessary). Set the selected flow rate with an accuracy of ±5 % using the calibrated flowmeter. Finally, turn off the pump and reseal the sampler.

9.3 *Collection of Samples:*

9.3.1 For personal monitoring, fix the sampler to the clothing of the worker, and place within the workers breathing zone (see Terminology D1356). Attach the sampling pump to the worker as appropriate, to minimize inconvenience. For fixed location sampling, select a suitable desired sampling site.

9.3.2 When ready to initiate sampling, remove the cover or plug from the inlet of the sampler and turn on the pump to begin sampling. Record the time and initial pump flow rate.

9.3.3 Since it is possible for filters to become clogged, monitor the performance of the sampler frequently, that is, a minimum of once per hour. Measure the flow rate with an accuracy of ±5 % using the calibrated flowmeter, and record the measured value.

9.3.4 At the end of the sampling period, terminate sampling, and measure the flow rate with an accuracy of ±5 % using the calibrated flowmeter. Consider the sample to be invalid if the flow rate was not maintained to within ±5 % of the nominal value throughout the sampling period. Record the volumetric flow rate and the time, and calculate the duration of the sampling period.

NOTE 20—If an integral timer is used, check the reading on the integral timer. Consider the sample to be invalid if this and the calculated sampling time do not agree to within ±5 %, since this suggests that the sampling pump was not operating throughout the entire sampling period.

9.3.5 Reseal the sampler and disconnect it from the sampling pump.

9.3.6 Record sample identity and all relevant sampling data. Calculate the average flow rate by averaging the flow rate measurements taken before and after (and perhaps during) the sampling period. Compute the volume of air sampled in litres by multiplying the mean flow rate (in L/min) by the sampling time (min).

9.3.7 For each batch of ten samples (or less), submit for analysis at least two unused filters (blanks) from the same lot used for sample collection. Subject these blank filters to exactly the same handling procedures as the samples, but draw no air through them.

9.4 *Transportation:*

9.4.1 For samplers having an internal filter cassette, remove the filter cassette from each sampler and place within a transport cover.

NOTE 21—Transport covers are normally supplied by the manufacturer

9.4.2 For samplers of the disposable cassette type, transport samples in the samplers from which they were collected.

NOTE 22—Samples may be placed in an ice cooler so that they are kept refrigerated during transport.

9.4.3 Samples shall be transported to the laboratory for analysis in such a manner to prevent contamination and damage to the samples in transit. Samples shall be individually and unambiguously labeled to ensure proper handling.

9.4.4 Avoid exposing filter samples to plasticizers that may cause reduction of Cr(VI).

9.4.5 Follow sampling chain of custody procedures in accordance with Guide D4840 to ensure sample traceability. Ensure that the documentation that accompanies the samples is suitable for a "chain of custody" to be established.

10. Preparation of Apparatus

10.1 *Cleaning of Glassware:*

NOTE 23—Perform all of the following while wearing gloves.

10.1.1 Before use, clean all glassware to remove any residual grease or chemicals by first soaking in laboratory detergent solution and then rinsing thoroughly with water.

10.1.2 After initial cleaning with detergent and water, clean all beakers with nitric acid. This can be accomplished by either soaking for a minimum of 24 h in concentrated nitric acid, or by the following procedure: fill beakers to one-third capacity with concentrated nitric acid, and then heat them at a hot plate surface temperature of 140°C in a fume hood until most of the liquid has evaporated, and allow to cool. Rinse beakers thoroughly with water.

10.1.3 Glassware that has been previously subjected to the entire cleaning procedure described in the previous steps, and which has been reserved for the analysis of hexavalent chromium, can be cleaned adequately by rinsing with nitric acid wash solution and then with water.

10.2 *Instrumental Set-Up:*

10.2.1 Set up the ion chromatograph in accordance with manufacturer's instructions.

10.2.2 Install the organic guard column and separator columns in the ion chromatograph.

10.2.3 Install a 1 mL sample loop on the injection valve of the ion chromatograph.

10.2.4 Adjust the eluant flow rate to that recommended by the manufacturer of the instrument. Increase the flow of the diphenylcarbazide (DPC) reagent solution until the flow rate reaches that recommended by the instrument manufacturer.

NOTE 24—It is recommended that the ratio of the flow rate of the DPC reagent solution to that of the eluent remain the same.

10.2.5 Measure the pH of the detector effluent, and ensure that the effluent pH is 2 (by addition of sulfuric or hydrochloric acid) or lower.

NOTE 25—pH needs to be strongly acidic to ensure a quantitative

reaction of DPC with Cr(VI).

10.2.6 Adjust the visible detector to read at 540 nm.

10.2.7 After the flow rates are adjusted, allow the system to equilibrate for at least 15 min.

11. Procedure

11.1 *Preparation of Sample and Blank Solutions*—Samples and blanks shall be prepared for subsequent analysis by using either a procedure for soluble hexavalent chromium or a procedure for insoluble hexavalent chromium. The former procedure entails extraction in water or sulfate buffer solution, while the latter involves hot plate digestion in carbonate extraction buffer solution.

NOTE 26—Perform all of the following while wearing gloves.

11.1.1 *Procedure for Soluble Hexavalent Chromium:*

NOTE 27—The following may be conducted using plastic labware.

11.1.1.1 Open each sampler or sample container, and transfer each filter sample or blank into a clean, labeled 50 mL beaker using nonmetallic flat-tipped forceps. If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the sampler form part of the sample, wash any particulate matter adhering to the internal surfaces into the beaker using a minimum volume of water (see 8.1.1) or extraction buffer (see 8.1.12.2).

11.1.1.2 Add ~6 mL of water (8.1.1; 8.1.12.2(1)) or ammonium sulfate/ammonium hydroxide extraction buffer (8.1.12.2(2)) to the beakers and swirl gently to mix the contents. Ensure that the sample-loaded sides of the filters remain completely immersed. Cover the beakers with watch glasses.

11.1.1.3 Allow the immersed filters to sit for one hour at room temperature, swirling/agitating occasionally.

NOTE 28—Alternative temperatures, for example, 37°C (**6**), may be used if desired.

11.1.1.4 Remove the filters from the beakers with flat-tipped forceps, carefully washing all surfaces with an additional 1 to 2 mL of water. Discard the filters.

11.1.1.5 Remove particles in the solutions by filtration or centrifugation.

11.1.1.6 Quantitatively transfer the solutions containing extracted soluble hexavalent chromium to 10-mL one-mark volumetric flasks. Rinse all surfaces with a minimum volume of water, and ensure that the rinsate is transferred to the volumetric flask.

11.1.1.7 Adjust the pH to 8 ± 0.2 with a minimum amount of buffer concentrate (2 M ammonium sulfate/1 M ammonium hydroxide). Account for any significant change in volume.

NOTE 29—This is needed for subsequent ion chromatographic analysis. The slightly basic nature of the solution stabilizes both Cr(III) and Cr(VI) species.

11.1.1.8 Dilute to the mark with water.

11.1.2 *Procedure for Total Hexavalent Chromium:*

NOTE 30—As an alternative to hot plate dissolution of Cr(VI), ultrasonic extraction may be used.

11.1.2.1 Open each sampler or sample container, and transfer each filter sample or blank into a clean, labeled 50 mL beaker using flat-tipped forceps. If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the sampler form part of the sample, wash any particulate matter adhering to the internal surfaces into the beaker using a minimum volume of extraction buffer solution (see 8.1.12.1).

11.1.2.2 Add 10 mL of extraction solution (8.1.12.1), 2 % (m/v) sodium hydroxide/3 % (m/v) sodium carbonate 0.05 (pH 13), to each beaker containing filter samples or blanks. Ensure that the filters are completely immersed in the extraction solution.

11.1.2.3 Place the beakers containing the filters and extraction solution on a hot plate that is preheated to a surface temperature of 135°C, and heat the solutions with occasional swirling for 60 to 90 min. Do not allow solutions to boil over or evaporate to dryness.

NOTE 31—Evaporation to dryness can cause unwanted interconversion of Cr(VI) and Cr(III) species. For example, aereal oxidation may cause oxidation of Cr(III) to Cr(VI).

11.1.2.4 Remove the beakers from the hot plate and allow them to cool to room temperature.

11.1.2.5 Carefully rinse each watch glass and the insides of each beaker with water, and transfer each solution quantitatively to a 10 mL one-mark volumetric flask. Remove any undissolved particulate by filtration or centrifugation.

11.1.2.6 Check the pH and, if necessary, adjust the pH to 13 ± 0.2 with a minimum amount of extraction solution (8.1.12.1) or sulfuric acid.

NOTE 32—It is important that the buffer solution be slightly basic, as this pH stabilizes both Cr(III) and Cr(VI) species.

11.1.2.7 Dilute to the mark with water.

11.1.3 *Procedure for Insoluble Chromium:*

11.1.3.1 If it is desired to determine insoluble Cr(VI), follow the above procedures for determining soluble Cr(VI) (11.1.1) and total Cr(VI) (11.1.2), respectively (in sequence).

11.1.3.2 Insoluble Cr(VI) is determined by the difference in results obtained for total Cr(VI) and soluble Cr(VI):
[Insoluble Cr(VI)] = [Total Cr(VI)] - [Soluble Cr(VI)].

11.2 *Instrumental Analysis:*

11.3 *Analysis of Calibration Solutions:*

11.3.1 Remove a portion (2-5 mL) of each calibration solution, and filter it through a 0.45 µm syringe filter.

11.3.2 Inject 1 mL of filtered calibration solution into the ion chromatographic system, using an appropriate syringe or auto sampler, into the eluant stream, and mark the injection time on the chromatogram recorder.

11.3.3 Determine the absorbance for hexavalent chromium response for each of the calibration standards, using either peak height (in absorbance) or peak area (peak magnitude × time) for the chromatographic peak assigned to hexavalent chromium. Also determine the absorbance at the retention time of hexavalent chromium of a reagent blank solution, consisting of a calibration solution matrix to which no hexavalent chromium has been added.

11.3.4 Prepare a calibration curve by using a linear plot of the peak height or area as a function of concentration of calibration solution by the regression analysis of least squares.

Correct for the absorbance of the reagent blank solution. The coefficient of determination (R^2) shall be greater than 0.99.

11.3.5 Prepare a new calibration graph whenever new reagents are used, new calibration solutions are prepared, hardware is altered, or continuing calibration varies from the initial calibration by more than 10 %.

NOTE 33—Many instruments prepare and statistically evaluate calibration graphs automatically. Thus the preparation of calibration graphs, and associated computations, need not be done manually.

11.4 *Analysis of Samples:*

11.4.1 Remove a portion (2-5 mL) of each sample solution (whether soluble or insoluble Cr(VI)), and each matrix blank solution, and filter it through a 0.45 µm syringe filter which is made of inert material (for example, PTFE).

11.4.2 Inject 1 mL of filtered sample solution into the ion chromatographic system, using an appropriate syringe or auto sampler, into the eluant stream, and mark the injection time on the chromatogram recorder. Also do the same for each matrix blank.

NOTE 34—All samples and standards need to be filtered before injection to avoid plugging columns and tubing.

11.4.3 Determine the absorbance for hexavalent chromium response for each of the sample solutions and matrix blanks, using either peak height or peak area for the chromatographic peak attributed to hexavalent chromium.

11.4.4 Determine the concentrations of hexavalent chromium in the sample solutions and matrix blanks by comparison with the calibration graph (absorbance or peak area vs. concentration of hexavalent chromium).

11.4.5 If concentrations of hexavalent chromium above the upper limit of linear calibration are found, dilute the sample test solutions in order to bring them within the range of the calibration, and repeat the analysis. Make all dilutions using the same buffer solutions as before, and record the dilution factor (DF).

NOTE 35—For samples expected to have very high concentrations of Cr(VI), dilution may be necessary before reacting with DPC. Otherwise, swamping of the DPC reagent can occur, and no color may develop.

11.5 *Estimation of the Instrumental Detection Limit (IDL):*

11.5.1 Estimate the instrumental detection limit under the working analytical conditions following the procedure described below, and repeat this exercise whenever the experimental conditions are changed.

11.5.1.1 Prepare test solutions at a concentration of 0.01 µg of hexavalent chromium per litre by diluting the Cr(VI) standard solution.

11.5.1.2 Make at least twenty ion chromatographic measurements on the test solution and calculate the instrumental detection limit as three times the sample standard deviation of the mean concentration value.

NOTE 36—The limit of detection calculated from results using this procedure is an instrumental detection limit. This is of use in identifying changes in instrument performance, but it is not a method detection limit. The instrumental detection limit is likely to be unrealistically low because it only takes into account the variability between individual instrumental readings; determinations made on one solution do not take into consideration contributions to variability from the matrix or sample.

11.6 *Estimation of the Method Detection Limit (MDL):*

11.6.1 Estimate the method detection limit (MDL) under the working analytical conditions following the procedure described in 11.6.2 and 11.6.3, and repeat this exercise whenever the experimental conditions are changed significantly.

11.6.2 Fortify at least ten filters (7.2) with hexavalent chromium near the anticipated detection limit, for example, 0.01 µg of Cr(VI), by spiking the filter with 0.1 mL of a suitable calibration solution (8.1.15.3) diluted by an appropriate factor with the desired extraction solution (8.1.12).

11.6.3 Make ion chromatographic/spectrophotometric measurements on the test solutions derived from each spiked filter (11.6.2) (after carrying out hot plate or ultrasonic extraction of the filters), and calculate the MDL as three times the sample standard deviation of the mean concentration value.

NOTE 37—An alternative procedure for estimating the method detection limit involves the analysis of filter samples fortified with the analyte of interest at values spanning the predicted MDL (**7**).

11.7 *Quality Control*—Quality control (QC) samples to be processed with each batch of field samples are summarized below.

11.7.1 *Reagent Blanks and Media Blanks:*

11.7.1.1 Carry reagent blanks (extraction solutions and reagents) and media blanks (unspiked filters) throughout the entire sample preparation and analytical process to determine whether the samples are being contaminated from laboratory activities. Process reagent and media blanks according to a frequency of at least 1 per 20 samples or a minimum of one per batch.

11.7.2 *Spiked Samples and Spiked Duplicate Samples:*

11.7.2.1 Process these samples on a routine basis to estimate the method accuracy on the sample batch, expressed as a percent recovery relative to the true spiked value. Spiked samples and spiked duplicate samples consist of filters to which known amounts of analyte were added. (This can be accomplished by spiking known volumes of known concentrations of Cr(VI) solutions at amounts within the dynamic range of the instrumentation. The Cr(VI) solution shall be prepared from a stock standard solution from a different source than that used for preparing the calibration solutions.) Process these QC samples at a frequency of at least 1 per 20 samples or minimum of one per batch.

11.7.2.2 Monitor the performance of the method by plotting control charts of the relative percent recoveries and of the relative percent differences between the spiked samples and the spiked duplicate samples. If QC results indicate that the method is out of control, investigate the reasons for this, take corrective action, and reanalyze the samples if possible. See Guide E882 for general guidance on the use of quality control charts.

11.7.3 *Certified Reference Materials (CRMs):*

11.7.3.1 Certified reference materials (CRMs) for hexavalent chromium shall be analyzed prior to routine use of the method, and periodically thereafter, to establish that the percent recovery relative to the certified value is satisfactory. Suitable CRMs are available from a few sources. A minimum of one CRM sample shall be analyzed at least six times quarterly.

11.7.4 *External Quality Assessment:*

11.7.4.1 If laboratories carry out Cr(VI) analysis on a regular basis, it is strongly recommended that they participate in a relevant external quality assessment scheme (for example, round-robin analysis) or proficiency testing scheme, if available.

12. Calculation

12.1 From the calibration graph, determine the mass of hexavalent chromium in each sample, W (µg), and in the average blank, B (µg).

12.2 Calculate the mass concentration of hexavalent chromium in the air sample, C (µg/m^3), in the air volume sampled, V (litres):

$$C = (W - B)/V \text{ , } \mu g/m^3.$$

If a dilution factor, DF, was used during determination of hexavalent chromium, the applicable computation is:

$$C = [(DF \times W) - B]/V, \mu g/m^3.$$

13. Report

13.1 The test report shall contain the following information:

13.1.1 A complete identification of the air sample, including: a) place of sampling; b) type of sample (personal or fixed location); c) date of sampling; d) personal identifier(s) for person(s) whose breathing zone(s) was (were) sampled (for personal samples) or the occupational environment sampled (for a fixed location sample).

13.1.2 A reference to this test method.

13.1.3 The name(s) (or alternative unique identifier(s)) of the person(s) conducting the sampling.

13.1.4 The type and diameter of filter used, and the type of sampler used. Also, report the type of sampling pump and its identification.

13.1.5 The type of flowmeter used, the primary standard against which it was calibrated, and the range of flow rates for which the flowmeter was calibrated.

13.1.6 The time at the start and end of the sampling period, and the duration of the sampling period in minutes. Also, report the flow rate at the start and end of sampling and the mean flow rate (in litres per minute).

13.1.7 Any interferants known to be present.

13.1.8 The time-weighted average mass concentration of hexavalent chromium found in each air sample (in µg Cr(VI)/m^3). Report the analytical variables used to calculate the result, including: a) the concentrations of hexavalent chromium in the sample and blank solutions; b) the volumes of the sample and blank solutions; and c) the dilution factor(s) used, if applicable.

NOTE 38—If necessary data (for example, sampling volumes) are not available to the laboratory for the above computations to be carried out, the laboratory report can contain the analytical hexavalent chromium results in units of micrograms of Cr(VI) per filter sample.

13.1.9 The type(s) of instrument(s) used for sample preparation and analysis, and unique identifiers(s). Report the estimated detection limit under the working analytical conditions.

13.1.10 Analytical results from quality control (QC) samples, for example, blanks, matrix spikes, and certified reference materials (CRMs).

13.1.11 Any operation not specified in this test method, is regarded as optional.

13.1.12 The name of the analyst(s) (or other unique identifier(s)), and report the date of the analysis.

13.1.13 Any inadvertent deviations, unusual occurrences, or other notable observations.

14. Precision and Bias

14.1 Method performance has been investigated using hot plate or ultrasonic extraction after collection onto polyvinyl chloride (PVC) filters. Analytical figures of merit from various tests are reported below.

14.1.1 *Sample Collection and Stability*—Laboratory testing with generated atmospheres of chromic acid mist yielded a collection efficiency of 94.5 % over the range 0.5 to 10 µg m^{-3} on 5-µm polyvinyl chloride (PVC) filters **(8)**; 96 % recovery of Cr(VI) was found two weeks after sample collection **(9)**. PVC filter samples generated from chromate-containing paint aerosols demonstrated no change in Cr(VI) recoveries after two weeks **(10)**. Long-term sample stability has been demonstrated for Cr(VI) in welding fume collected on binder-free quartz fiber filters **(11)**. Cellulose filters and at least one type of PVC filter have been shown to cause reduction of Cr(VI) over time **(12, 13)**. Rapid reduction of Cr(VI) has been observed in certain work environments, for example, plating works **(14)**, and filters may be treated with base in order to minimize this reduction **(3)**.

14.1.2 *Hot Plate Extraction*—Quantitative recoveries have been obtained for both soluble and insoluble chromates using sodium carbonate/sodium bicarbonate or hydroxide buffers **(15, 16)**. Negligible biases were found, and overall accuracies were ±12.9 % for the former buffer **(15)** and ±16.5 % for the latter **(16)**. Method detection limits (MDLs) for the former and latter buffers were found to be 0.01 and 0.02 µg of Cr(VI) per filter, respectively. Recoveries of Cr(VI) from a certified reference material (CRM) generated from welding dust were quantitative for both buffer solutions **(16, 17)**. The applicable range is the MDL (0.001 µg m^{-3}) to at least 800 µg Cr(VI) m^{-3} **(16)**.

14.1.3 *Ultrasonic Extraction*—Quantitative recoveries have been obtained for soluble chromates using ammonium sulphate/ammonium hydroxide buffer **(18, 19)**. Negligible biases were found, and overall accuracy was ±16.8 %. The method detection limit (MDL) when using a solid-phase extraction procedure to isolate Cr(VI) was estimated to be 0.09 µg Cr(VI) per filter **(18)**, but the MDL for ion chromatographic isolation is probably lower (but has not yet been evaluated). Recoveries of Cr(VI) from a certified reference material (CRM) generated from welding dust were quantitative**(16, 18)**. The applicable range is from the MDL (~0.01 µg m^{-3}) to at least 800 µg Cr(VI) m^{-3} **(16, 20)**.

14.1.4 *Sequential Extraction of Soluble and Insoluble Chromates*—Sequential extraction procedures for determining soluble and insoluble Cr(VI) species in workplace air samples were evaluated **(21)**. Two-step extraction involving either water or sulfate buffer for the dissolution of soluble Cr(VI) compounds, followed by sonication in carbonate buffer to obtain insoluble Cr(VI) species, yielded results that demonstrated acceptable performance. That is, on samples dosed with

known amounts of soluble and insoluble Cr(VI) compounds, quantitative recoveries of soluble species were obtained from soluble extraction, and quantitative recoveries of insoluble species were obtained by insoluble extraction (after the soluble extraction method was first carried out). However, three-step extraction (with first water, then sulfate buffer, and lastly carbonate buffer) resulted in partial dissolution of sparingly soluble Cr(VI) species by water during the first step of the sequence. Applications of sequential extraction procedures to paint pigment samples and to stainless steel welding fume samples were also successfully demonstrated (**21**).

15. Keywords

15.1 hexavalent chromium; workplace atmospheres; ion chromatography; spectrophotometry

APPENDIX

(Nonmandatory Information)

X1. SAMPLER WALL DEPOSITS (22, 23)

X1.1 Samplers for aerosols typically consist of a filter supported in a holder, though other collection substrates are also used, for example, impaction plates, and foams. The entire device is considered to be an aerosol sampler. The sampling efficiency of the aerosol sampler is considered to be the air concentration calculated from the particles collected by the sampler compared to the undisturbed concentration in air. All aerosol samplers exhibit a decrease in sampling efficiency with increasing particulate aerodynamic diameter. Some size-selective samplers are designed for a specific sampling efficiency over a range of aerodynamic diameters, in which case the actual sampling efficiency of the sampler is considered in reference to the stated efficiency. In some sampler designs (for example, cyclones) there is an internal separator to achieve the required size separation.

X1.2 The collection efficiency of an aerosol sampler has three components: aspiration (or entry efficiency), passage within the sampler (either from entry plane to collection substrate or, if an internal separator is present, both from entry plane to internal separator and from internal separator to collection substrate) and penetration (through the internal separator, if present). For any given design of sampler, the three components are functions of particle aerodynamic size and air flow-rate through the sampler. The aspiration efficiency also depends on wind speed and direction, while the sampler's angle to the vertical influences both aspiration and transport efficiency. Part of the sample will deposit on internal surfaces of the sampler as a result of losses during passage within the sampler. In addition, if the sampler is transported after sampling, particles already deposited on the substrate may become dislodged and add to deposits already on the internal surfaces (although this is likely of lesser importance). If the design specification for the sampler is to include all aspirated particles, these losses should be taken into account unless it can be shown that they can be disregarded. Table X1.1 provides median and maximum values of deposits on the walls for two commercially available samplers in common use. No pattern can be discerned from these data that would allow the use of correction factors without introducing a very large uncertainty.

TABLE X1.1 CFC Maximum and Median Cr(VI) Wall Deposits (22)

Environment	n	Maximum wall deposit (%)	Median wall deposit (%)
Welding	10	55	5
Plating	12	17	12
Paint spray	29	12	7

X1.3 For some samplers, the sample deposited on the collection substrate is considered to be the entire sample; that is, there are no wall deposits. For other samplers, it is recommended that the wall deposits be evaluated (**24**).

X1.4 There exist several procedures that could be used to account for wall deposits. One method is digestion within the body of the sampler, which is the practice in some French standard methods. This procedure needs to be carefully designed with respect to the composition of the extraction media, the composition of the substrate and the stability and integrity of the sampler. Another procedure, often followed, is to rinse the internal deposit into the digestion vessel containing the collection substrate. This may be quantitative if the deposit is very soluble or easily displaced, but that may not be the case, even when acid is used for the rinse. Brushing the deposit into the digestion vessel may not be quantitative, and may be a source of contamination. A procedure that has been tested in a limited evaluation and shown to be quantitative is wet-wiping of the internal surfaces.

X1.5 Wiping the internal surfaces of a sampler with a wetted wipe allows a combination of mechanical removal with wetting or solubilization. The choice of wipe is important. It must be free of significant contamination, and it must be compatible with the digestion and analytical procedure. The area of the wipe should be as small as possible in order not to unduly compromise the detection limits of the analysis, and quality control samples should be matched to the same matrix. Typically, the same material should be used as would be selected to perform a surface wipe sample for the element(s) of interest. If the most appropriate wipe material cannot be digested and analyzed in the same way as the collection substrate, it can be analyzed as a separate sample and the results combined. Where the procedure has not been validated to provide quantitative results for a first wipe, the analysis of a second wipe can be used as a guide to recovery.

X1.6 Where the validation of an air sampling and analytical method has not included a specific procedure for recovering and analyzing wall deposits, any procedure selected for this purpose will add an unknown amount to the uncertainty budget of the method. It is therefore recommended that any procedure be validated to determine the contribution to uncertainty.

REFERENCES

(1) (a) Agency for Toxic Substances and Disease Registry (ATSDR), *Toxicological Profile for Chromium*, ATSDR, Atlanta, GA, USA, 2000; (b) International Agency for Research on Cancer (IARC), *Monographs on the Evaluation of Carcinogenic Risks to Humans—Chromium, Nickel and Welding (Vol. 49)*, IARC, Lyon, France, 1990; (c) National Institute for Occupational Safety and Health (NIOSH), *Criteria for a Recommended Standard—Occupational Exposure to Hexavalent Chromium*, NIOSH, Cincinnati, OH, USA, 2013, [DHHS (NIOSH) Publ. No. 2013–128].

(2) Occupational Safety and Health Administration (OSHA), *OSHA Regulatory Agenda - Occupational Exposure to Hexavalent Chromium (Prevention Occupational Illness—Chromium)*; OSHA, Washington, 1998.

(3) Health and Safety Executive (HSE), *Methods for the Determination of Hazardous Substances*, MDHS methods 52/3 and 61; HSE Books, Sudbury, UK, 1998.

(4) Molina, D., Abell, M., "An Ion Chromatographic Method for Insoluble Chromates in Paint Aerosol," *American Industrial Hygiene Association Journal*, Vol 48, 1987, pp. 830–835.

(5) Zatka, V., "Speciation of Hexavalent Chromium in Welding Fumes—Interference by Air Oxidation of Chromium," *American Industrial Hygiene Association Journal*, Vol 46, 1985, pp. 327–331.

(6) Ashley, K., "International Standard Procedure for the Extraction of Metal Compounds Having Soluble Threshold Limit Values," *Applied Occupational and Environmental Hygiene*, Vol 16, 2001, pp. 850–853.

(7) Kennedy, E. R., Fischbach, T. J., Song, R., Eller, P. M., and Shulman, S., "Guidelines for Air Sampling and Analytical Method Development and Evaluation," NIOSH: Cincinnati, OH, USA, 1995.

(8) NIOSH/OSHA, *Occupational Health Guidelines for Chemical Hazards: Occupational Health Guidelines for Chromic Acid and Chromates*, U.S. Department of Health and Human Services (NIOSH) Publ. No. 81-123, NIOSH: Cincinnati, OH, USA, 1981.

(9) *NIOSH Manual of Analytical Methods*, 2nd ed., Vol 1; Method P 169, U.S. Department of Health, Education, and Welfare (NIOSH) Publ. No. 77-157-A. NIOSH: Cincinnati, OH, USA, 1977.

(10) *NIOSH Manual of Analytical Methods*, 4th ed., Method No. 7604, U.S. Department of Health and Human Services (NIOSH) Publ. No. 94-113, NIOSH: Cincinnati, OH, USA, 1994.

(11) Dyg, S., Anglov, T., and Christensen, J. M., "Preparation of Filters Loaded with Welding Dust—A Homogeneity and Stability Study of Hexavalent Chromium," *Analytica Chimica Acta*, Vol 286, 1994, pp. 273–282.

(12) Blomquist, G., Nilsson, C.-A., and Nygren, O., "Sampling and Analysis of Hexavalent Chromium During Exposure to Chromic Acid Mist and Welding Fumes," *Scandinavian Journal of Work, Environment, and Health*, Vol 9, 1983, pp. 489–495.

(13) Spini, G., Profumo, A., Riolo, C., Beone, G. M., and Zecca, E., "Determination of Hexavalent, Trivalent and Metallic Chromium in Welding Fumes," *Toxicological and Environmental Chemistry Journal*, Vol 41, 1994, pp. 209–219.

(14) Foster, R. D., Howe, A. M., Cottrell, S. J., and Northage, C., "An Investigation of the Exposure of Workers to Hexavalent Chromium in the Air of Plating Works," HSL Report IR/L/95/15. Health and Safety Laboratory, Sheffield, UK, 1996.

(15) OSHA, "Hexavalent Chromium in Workplace Atmospheres," Method No. ID-215; in *OSHA Analytical Methods Manual*, 2nd ed. OSHA: Salt Lake City, UT, 1993.

(16) Boiano, J. M., Wallace, M.E., Sieber, W. K., Groff, J. H., Wang, J., and Ashley, K., "Comparison of Three Sampling and Analytical Methods for the Determination of Airborne Hexavalent Chromium," *Journal of Environmental Monitoring*, Vol 2, 2000, pp. 329–333.

(17) Vercoutere, K., Cornelis, R., Dyg, S., Mees, L., Christensen, J. M., Byrialsen, K., Aaen, B., and Quevauviller, P., "Cr(III) and Cr(VI) Speciation Measurements in Environmental Reference Materials," *Microchimica Acta*, Vol *123*, 1996, pp. 109–117.

(18) Wang, J., Ashley, K., Marlow, D., England, E., and Carlton, G., "Field Method for the Determination of Hexavalent Chromium by Ultrasonication and Strong Anion-exchange Solid-phase Extraction," *Analytical Chemistry*, Vol 71, 1999, pp. 1027–1032.

(19) Wang, J., Ashley, K., Kennedy, E. R., and Neumeister, C., "Determination of Hexavalent Chromium in Industrial Hygiene Samples Using Ultrasonic Extraction and Flow Injection Analysis," *Analyst*, Vol 122, 1997, pp. 1307–1312.

(20) Marlow, D., Wang, J., Wise, T. J., and Ashley, K., "Field Test of a Portable Method for the Determination of Hexavalent Chromium in Workplace Air," *American Laboratory*, Vol 32, No. 15, 2000, pp. 26–28.

(21) Ashley, K., Applegate, G. T., Marcy, A. D., Drake, P. L., Pierce, P. A., Carabin, N., and Demange, M., "Evaluation of Sequential Extraction Procedures for Soluble and Insoluble Hexavalent Chromium Compounds in Workplace Air Samples," *Journal of Environmental Monitoring*, Vol 11, 2009, pp. 318–325.

(22) Harper, M. and Demange, M., "Concerning Sampler Wall Deposits in the Chemical Analysis of Airborne Metals," *Journal of Occupational and Environmental Hygiene*, Vol 4, 2007, pp. D81–D86.

(23) Demange, M., Gendre, J. C., Hervé-Bazin, B., Carton, B., and Peltier, A., "Aerosol Evaluation Difficulties Due to Particle Deposition on Filter Holder Inner Walls," *Annals of Occupational Hygiene*, Vol 34, 1990, pp. 399–403.

(24) Ashley, K., and Harper, M., "Closed-Face Filter Cassette (CFC) Sampling—Guidance on Procedures for Inclusion of Material Adhering to Internal Sampler Surfaces," *Journal of Occupational and Environmental Hygiene*, Vol 10, 2013, pp. D29–D33.